

PS-PMMA blends studied by X-ray spectromicroscopy

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INTRODUCTION

Blends of polystyrene (**PS**) and poly(methyl methacrylate) (**PMMA**) are classic model systems in polymer science. We selected this system as a possible means to make a relatively flat model surface with alternating hydrophilic and hydrophobic domains, in the context of our exploration of scanning transmission X-ray microscopy (STXM) [1] and X-ray photoelectron emission microscopy (X-PEEM) [2] as tools to study competitive protein adsorption, a possible route to development of improved blood-contact biomaterials [3]. PS and PMMA are immiscible and readily phase separate in the bulk [4]. Since the interfacial tension between them is larger than the difference in their surface tensions, the two materials should have a strong tendency to extend the bulk phase segregation right to the surface.

Optical and scanning probe microscopy studies of dewetting of a PS overlayer deposited on a PMMA underlayer [5] and STXM and scanning force microscopy (SFM) of phase segregation upon annealing a 50/50 27K/27K PS/PMMA blend [6] both suggested that it would be straightforward to create the desired surface from spun cast PS/PMMA blends. We started our work in June 2000 with X-PEEM studies of PMMA-rich PS/PMMA thin film blends made from mono-disperse high Mw polymers. We were surprised to find that, although the bulk had the expected phase segregated morphology [5,6], there was a strong PS-like signal in the NEXAFS spectrum of the surface region of the PMMA domains. On reviewing the literature we found a very conflicting set of articles dealing with surface composition of PS/PMMA blends. Tanaka et al. [7] gave clear evidence that PS segregates preferentially to the surface on as-prepared PS/PMMA blends cast on Si wafers. Other studies showed that PMMA can surface

segregate under certain circumstances [8-10]. In order to work toward our goal of forming the desired model surface, we have carried out a series of measurements aimed at better understanding how film fabrication, thermodynamics, and kinetics determine the surface and bulk morphology of PS/PMMA blends. In doing so, we have found that STXM and X-PEEM at the ALS combined with lab based AFM and XPS measurements, gives good insight into the bulk and surface film structure of polymer blends.

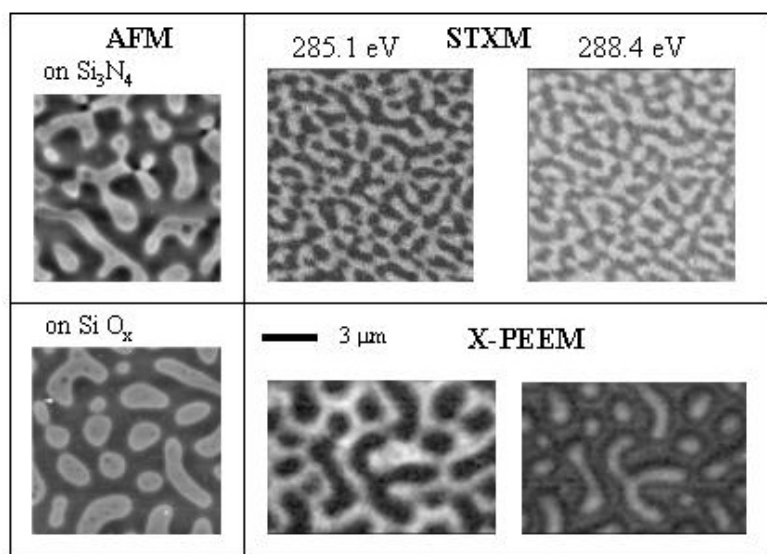


Fig. 1 AFM, STXM and XPEEM images (at 285.1 and 288.4 eV) of annealed 30/70 PS/PMMA blend made from 1060K/312K Mw species.

Thin (30-100 nm) films of blends of PS/PMMA with compositions ranging from 10/90 to 33/66 were made from relatively high Mw (1030 K/300K) mono-disperse pure materials. The samples were annealed with various protocols - details of ingredients, sample preparation and annealing are given elsewhere [11]. The annealing temperatures (in all cases significantly above the T_g of PS or PMMA) and times were sufficient to reach equilibrium structures in films made with low Mw components but probably not for high Mw materials. As-made and annealed films spun cast on Si₃N₄ windows were used for the STXM studies while as-made and annealed films spun cast on Si wafers with native oxide were used for the X-PEEM studies. AFM height and phase mode images were recorded on all materials to provide higher spatial resolution surface imaging as well as to quantify film thickness (scratch method) and surface roughness.

RESULTS AND DISCUSSION

Fig. 1 compares AFM height mode images of annealed 30/70 (wt%/wt%) PS/PMMA films, with STXM and X-PEEM images of the same films recorded at 285.1 eV, the energy of the $\pi^*_{C=C}$ of PS and at 288.4 eV, the energy of the $\pi^*_{C=O}$ of PMMA. The contrast reversal with the change in photon energy immediately identifies the domains. From STXM, the bulk has a volume ratio of the two domains close to that of the starting composition of the casting solution (30/70). However the X-PEEM and AFM show that the surface has an area ratio close to 50/50, indicating surface enrichment of PS [11]. Some average PS enrichment is not surprising, since the PMMA has a strong preference for SiO_x substrates. Typically, in phase segregating blends one expects the continuous phase to be the majority species. On this basis, AFM alone would mis-identify the phases since the X-PEEM clearly shows that the continuous phase is PS. Another surprise is that the PMMA domains protrude from the surface (white in the AFM image), even though the PS is surface segregated. Prior work found PS forming protruding structures [5,6].

Fig 2 compares AFM images and color-coded component maps for as-made and annealed 30/70 PS/PMMA derived from STXM and X-PEEM image sequence measurements

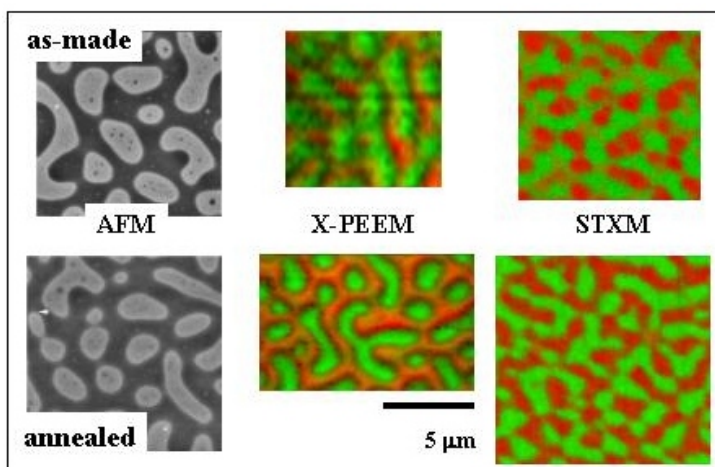


Fig. 2 Comparison of AFM with color coded component maps [11, 12] derived from STXM and X-PEEM of the as-made and annealed (140C, 2 hrs) 30/70 (1060K / 312K) PS/PMMA films.

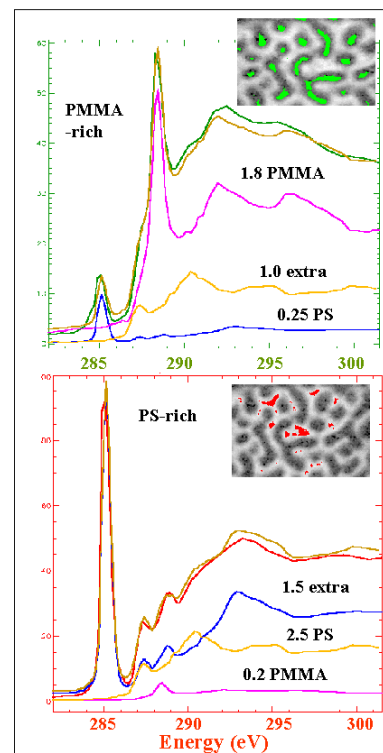


Fig. 3 Curve fit of the C 1s NEXAFS of the PMMA and PS domains of an annealed 30/70 PS/PMMA film (140C, 2 hrs).

[12]. Changes in morphology with annealing are seen clearly in the STXM mapping, but are much less pronounced in X-PEEM and negligible in AFM. The annealing protocol used (140°C, 2 hours, vacuum) induced lateral re-organization. However the PMMA domains showed PS at the surface before and after annealing, according to the X-PEEM NEXAFS spectra (**Fig. 3**).

In order to better understand the apparent discrepancy between the 30/70 PS/PMMA results and the earlier work, we also examined 50/50 PS/PMMA samples made with lower Mw (21K/22K) and more aggressive annealing, like those of the original STXM study [6]. These samples have the PS ball morphology found earlier [5,6]. Yet the X-PEEM spectra clearly show that PS is present in the continuous PMMA domain (**Fig. 4**). This result has been repeated twice, on both blends and dewetted bilayers, with similar results. At present there are a number of possible explanations for the apparently persistent surface PS-like signal:

- unresolved fine droplets of PS at the surface of the PMMA domains. These have been seen in high resolution STXM and lateral force microscopy. However they are not seen in the AFM recorded on the annealed 30/70 sample, even though small PS drops are seen in the as-made 30/70 sample.
- modification of the phase segregation process by the presence of a third component. A surface impurity, possibly a silicone, is suspected to exist - an extra component is needed to explain measured spectra (Fig. 3), or
- an as-yet un-identified aspect of the system leading to a strong preference for PS surface segregation.

We cannot provide a definitive answer at this time, but present these results both as a progress report and to illustrate the complementary strengths of AFM, STXM and X-PEEM. We hope these tools can be used to develop an in-depth understanding of bulk and surface phase segregation in this system and thus enable us to prepare the desired, phase segregated model surface, if this is possible. *Watch this channel same time next year !!*

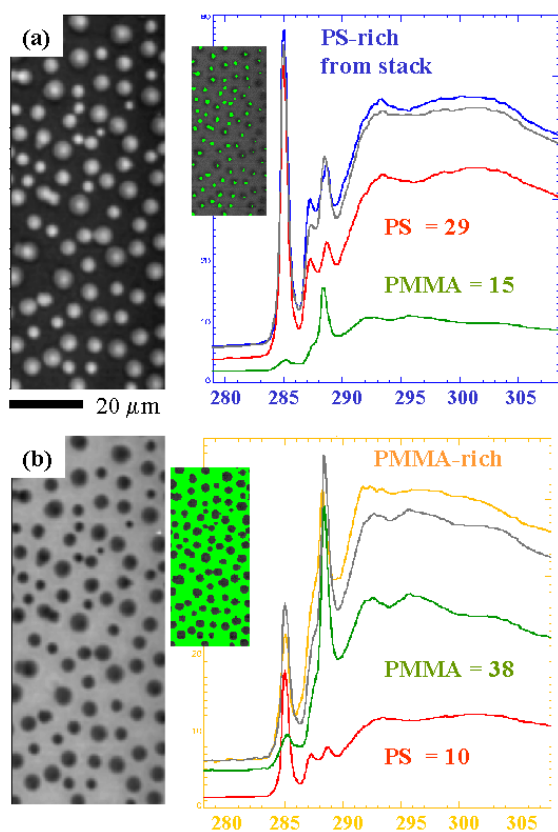


Fig. 4 Component maps and fitted spectra for a 50/50 PS/PMMA blend made from 21K/22K low Mw materials, and annealed for 48 hours at 165 C.

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